

In order to check this, we benzoylated 39 g. of our product and separated the isomers. We obtained 5 g. of the crystalline benzoate (from 1-3 ethylidene glycerol) m.p. 86°C, and 18 g. of the liquid benzoate (from 1-2 ethylidene glycerol), b.p. 163°C. 11 mm. The ratio of the two isomers is then 1:3.6 or our product consists of 78 per cent 1-2 ethylidene glycerol (I) and 22 per cent 1-3 ethylidene glycerol (II).

Formation of (I) is thus shown to be favored by the use of fluo-acid catalyst and by keeping the liquid cool during the reaction.

CUPROUS CHLORIDE AS A CATALYST FOR ACETYLENE.

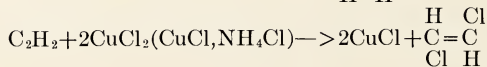
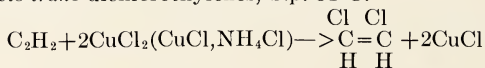
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Neutral or acid solutions of cuprous chloride and alkali chlorides or ammonium chloride absorb acetylene, forming several derivatives according to conditions. Intermediate products are probably formed, the final products being given off when the mixture is heated.

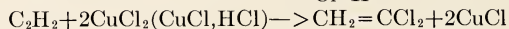
When cuprous and ammonium chlorides are used in solution saturated with hydrogen chloride gas, vinyl chloride is formed in about 30 per cent yield. The addition of an organic solvent is necessary to keep the very volatile vinyl chloride in solution.



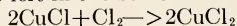
A mixture of cupric, cuprous and ammonium chlorides acts as a chlorinating agent. Acetylene passed into this solution forms the equilibrium mixture of *cis* and *cis-trans* dichlorethylenes, b.p. 54°C.



Cuprous and cupric chlorides, with or without ammonium chloride saturated with hydrochloric acid, give on treatment with acetylene a mixture of unsymmetrical and *cis-trans* dichlorethylenes. This is interesting as being the only synthesis which gives one of the symmetrical compounds without the other, also in that an unsymmetrical chlorination product is formed from a symmetrical hydrocarbon. The unsymmetrical dichlorethylene is identified by its boiling point (37°C.) and from its forming chloracetyl chloride and a solid polymerized product on standing in contact with air. The *cis-trans* compound is identified by its boiling point (48°C.). The *cis* isomer, b.p. 60°C., is not present.



After the products have been removed by heating, cupric chloride is regenerated by passing chlorine into the solution. Some cuprous chloride must be left in the solution for catalysis.



Solutions of cupric chloride in the absence of cuprous chloride do not absorb acetylene.

The mechanism of these reactions is unknown and will probably remain so until the constitution of chlorocupric acid (HCuCl_3 or $\text{CuCl}_2 \cdot \text{HCl}$) and chlorocuprous acid (H_2CuCl_3 or $\text{CuCl} \cdot 2\text{HCl}$) is more fully understood.